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JOSEPH A. HOLMES, DIRECTOR that the molecular volumes of ALL GASES ARE ALIKE BY

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# ERRORS IN GAS ANALYSIS DUE TO ASSUMING THAT THE molecular volumes of all gases are alike. 

By George A. Burrell and Frank M. Seibert.

## INTRODUCTION.

The Bureau of Mines in the course of various investigations has sampled and analyzed the gases found in coal and metal mines, those that flow from wells in oil and gas fields, and those produced during the processes of combustion in furnaces. In determining the purity of certain combustible gases by the method of slow combustion, the authors found that in some analyses the volume of carbon dioxide and the contraction produced by the combustion did not agree with the theoretical value, according to the equations ordinarily used for showing the reaction. Also, in analyzing some natural gases by the same method the paraffin hydrocarbons present totaled over 100 per cent. The differences were greatest when the oxygen taken was only a few cubic centimeters in excess of that required to burn the gas completely. The variations could not be attributed to experimental errors, because all the analyses were carefully performed in duplicate and the gas burettes were accurately calibrated. Consequently, an inquiry was made to determine the errors that might arise in the combustion method of analysis by assuming that the molecular volume (the quotient of the molecular weight divided by the density) is the same for every gas. This paper presents the results of that inquiry, and is published by the Bureau of Mines because these results show the need of applying corrections in some exact analyses of certain gases by the combustion method.

In working out the results, the authors wish to acknowledge the valuable assistance of G. A. Hulett, chief chemist of the bureau.

## DEDUCTIONS OF WOHL AND HABER.

Wohl ${ }^{a}$ has shown that the errors due to the assumption stated are considerable, but the authors of this paper are not entirely in accord with some of his deductions. Wohl derives expressions for the molecular volumes from determinations taken from a table given by Nernst. ${ }^{b}$ These values agree closely with the latest determinations

[^0]except in the case of methane. The value for methane is given as 1.002 at $0^{\circ} \mathrm{C}$. and 760 mm . Baumé and Perrot found it to be 0.999 , as shown in the table of specific gravities given on page 9 of this paper.

Wohl's gas-analysis apparatus differs from the one used in the work herein reported in that his measurements were made at constant volume instead of constant pressure. Wohl made the mistake of assuming that the expressions he derived as showing the exact proportions of certain gases entering into reaction with each other could be used in all cases. The fact is that his equations apply only when the carbon dioxide produced by the combustion constitutes between 95 and 100 per cent of the total quantity of gases remaining after combustion. It is true, as he stated, that in the case of hydrogen, carbon monoxide, and methane the quotient of the molecular weight divided by the density at $0^{\circ} \mathrm{C}$. and 760 mm . (the molecular volume) approximates very closely the value 22.412 for an ideal gas, but in the case of carbon dioxide the value becomes 22.268. He therefore concludes that Avogadro's theory does not hold in this case.

Haber ${ }^{a}$ does not consider Wohl's conclusions valid. He demonstrates his objection as follows:

From Van der Waals's equation, the ratio between the pressure $P$, the volume $V$, and the temperature $T$ of a gas is expressed thus:

$$
\left(P+\frac{a}{V^{2}}\right)(V-b)=R T
$$

Further, if $d=$ density at $0^{\circ} \mathrm{C}$. and 760 mm . pressure, and $M$ the molecular weight the following equation is derived:

$$
\frac{M}{d}=(1+a)(1-b)=R
$$

For carbon dioxide Van der Waals gives the following values:

$$
\begin{aligned}
& a=0.00874 \\
& b=0.00230
\end{aligned}
$$

Therefore $\left(\frac{M}{d}\right) 1.00646=R=22.412$
The value $\frac{M}{d}=22.268=$ volume of a gram molecule

$$
\text { then } \frac{22.268}{22.412}=\frac{\text { molecular volume of carbon dioxide }}{\text { molecular volume of oxygen }}
$$

This value is the same as that obtained by dividing the theoretical specific gravity by the observed specific gravity.

Haber therefore concludes that the deviation in the case of carbon dioxide is due only to the fact that at $0^{\circ} \mathrm{C}$. and 760 mm . pressure carbon

[^1]dioxide is not a perfect gas and that the deviation has nothing to do with Avogadro's theory. Haber further shows from Van der Waals's equation that when $V$ is large the term $\frac{a}{V^{2}}$ is negligible and that the difference between $V$ and $(V-b)$ is also negligibly small. The equation then becomes
$$
P V=R T=C
$$

Hence, as the partial pressure of a gas decreases from 1 atmosphere, the gas will more nearly behave like an ideal gas, or, in other words, there can be obtained some partial pressure at and below which the behavior of the gas will differ so slightly from that of an ideal gas that the deviation will be negligible in eudiometry. This partial pressure can be obtained by diluting the gas whose behavior deviates from that of an ideal gas with one, or a mixture of two or more gases, whose behavior at $0^{\circ}$ and 760 mm . pressure is sufficiently close to that of a perfect gas. Air, the chief constituents of which are oxygen and nitrogen, can be used.

In view of these facts Haber concludes that in order to avoid the use of corrected equations in calculating the percentages of combustible gases from the combustion data afforded by a gas analysis, such a small quantity of the combustible gas should be taken for the analysis that the carbon dioxide produced by the combustion does not exceed 30 per cent of the total quantity of gas measured; that is, its partial pressure should not exceed 30 per cent of the total pressure after combustion.

## AUTHORS' COMMENTS ON WORK OF WOHL AND HABER.

In summing up the work of Wohl and Haber regarding the true molecular volume of gases the authors of this paper comment as follows:
(1) In exact gas analysis by slow combustion, Wohl's observation that the combustion data must be corrected when the partial pressure of the carbon dioxide produced is high has been confirmed.
(2) The authors agree with Haber that Wohl's expressions can be used only in special cases when the partial pressure of the carbon dioxide constitutes nearly 100 per cent of the total pressure.
(3) The authors disagree with Haber's conclusion that the best method of making combustion analyses is to keep the partial pressure of the carbon dioxide so low (less than 30 per cent of the total pressure) in the gases measured after the combustion as to eliminate the use of corrected equations. Their conclusion is reached by reasoning as follows:

SOURCES OF ERROR IN GAS ANALYSES.
In the analyses of some mixtures rich in combustible gases so small a proportion of the original gas has to be used in order to keep the partial pressure of the $\mathrm{CO}_{2}$ produced below 30 per cent that a small
error of manipulation is magnified many times when the calculation to a percentage basis is made. In many forms of gas-analysis apparatus such errors are unavoidable, and even in the use of apparatus designed for exact work they occur to some extent.

The point is illustrated by the following data relating to an analysis of natural gas by the explosion method. For the analysis only a small proportion of the sample was taken.

## Analysis of a sample of natural gas by the explosion method.

Cubic centimeters.
Volume of sample taken.................................................... 7.0
Volume after carbon-dioxide absorption........................................... 7.0
Air added......................................................................... 93.0
Total volume. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 100.0
Volume after explosion............................................................ 85.5
Contraction........................................................................... 14.5
Volume after absorption of carbon dioxide..................................... 77.3
Carbon dioxide produced.......................................................... 8.2

$$
\begin{aligned}
\text { If } x & =\text { partial methane } \\
\text { and } y & =\text { partial ethane, } \\
\text { Then } 2 x+2.5 y & =14.5, \\
x+2 y & =8.2 . \\
\text { From which } x & =5.68, \\
y & =1.26, \\
\mathrm{CH}_{4} & =81.1 \text { per cent, } \\
\mathrm{C}_{2} \mathrm{H}_{6} & =18.0 \text { per cent, } \\
\text { Total paraffins } & =99.1 \text { per cent. }
\end{aligned}
$$

If one makes an error of, say, +0.1 c. c.in reading the volume after explosion and an error of -0.1 c. c. in reading the carbon-dioxide absorption, the figures become:

$$
\begin{aligned}
2 x+2.5 y & =14.4 \\
x+2.0 y & =8.4 \\
x & =5.2 \\
y & =1.6 \\
\text { Percentage of } \mathrm{CH}_{4} & =74.3
\end{aligned}
$$

$$
\text { Percentage of } \mathrm{C}_{2} \mathrm{H}_{6}=22.8
$$

Percentage of total paraffins $=97.10$, or a difference of 2 per cent.
The results of an analysis of a sample of methane by the explosion method are also illustrative.

## Analysis of a sample of pure methane.

Cubic centimeters.
Volume of sample taken ..... 8.0
Volume after carbon-dioxide absorption ..... 8.0
Air added ..... 92.0
Total volume ..... 100.0
Volume after explosion ..... 84.0
Contraction ..... 16.0
Volume after absorption of carbon dioxide ..... 76.0
Carbon dioxide produced ..... 8.0

If an error of $\pm 0.1$ c. c. be made in reading the volume after the carbon-dioxide absorption, then hydrogen, carbon monoxide, or some hydrocarbon other than methane is indicated. If instead of the carbon dioxide reading being 8 , it was 7.9 , then instead of the methane calculating to 100 per cent, it would calculate to only 98.7 per cent-a difference of 1.3 per cent. Therefore if one were examining a gas for its purity one could not be sure whether or not there was some other gas present, at least to the extent of 1 per cent.

In many cases, however, the partial pressure of the carbon dioxide can be kept low, the use of corrected equations being thus avoided. At the same time such a quantity of the sample can be used for analysis as not to increase the experimental error appreciably. For instance, the partial pressure of the carbon dioxide can be kept low in mixtures containing small proportions of methane, carbon monoxide, ethane, coal gas, blast-furnace gas, or producer gas. But for mixtures in which the carbon gases constitute almost the whole of the sample it is much better to use the slow-combustion method, taking such a quantity of the sample that the oxygen added for combustion will be only a few cubic centimeters in excess of that theoretically required and applying corrected equations.

## RECENT SPECIFIC-GRAVITY AND MOLECULAR-VOLUME DETERMINATIONS.

Tables ${ }^{a}$ of recent specific-gravity determinations (at $0^{\circ} \mathrm{C}$. and 760 mm . pressure) for different gases and of the molecular volumes of carbon dioxide and ethane at various partial pressures are presented below:

Results of specific-gravity determinations of various gases.

| Gas. | Molecular weight. | Specific gravity.$(\mathrm{Air}=1 .)$ |  | Observer. | $\frac{\text { Theoretical }}{\text { Observed. }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Theoretical. | $\mathrm{Ob}-$ served. |  |  |
| $\mathrm{CH}_{4}$ | 16. 03 | 0.5538 | 0.5545 | Baumé and Perrot. | 0.999 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | 30.05 | 1.0381 | 1. 0494 | -...do.............. | 0.990 |
| CO.. | 28.00 | 0.9673 | 0.9670 | Leduc. | 1. 000 |
| CO. | 28.00 | 0.9673 | 0.9672 | Rayleigh | 1. 000 |
| $\mathrm{CO}_{2}$ | 44.00 | 1. 5201 | 1. 5287 | Leduc.. | 0.994 |
| $\mathrm{CO}_{2}$ | 44. 00 | 1.5201 | 1.5291 | Rayleigh. | 0.994 |
| $\mathrm{N}_{2}$. | 28.02 | 0.9680 | 0.9674 | - ...do. | 1. 001 |
| $\mathrm{N}_{2}$ | 28.02 | 0.9680 | 0.9672 | Leduc. | 1. 001 |
| $\mathrm{O}_{2}$ | 32.00 | 1.1055 | 1. 1054 | Rayleigh | 1. 000 |
| $\mathrm{O}_{2} \ldots$ | 32.00 | 1. 1055 | 1.1052 | Leduc. | 1.000 |
| $\mathrm{C}_{2} \mathrm{H}_{4} .$ | 28.03 | 0.9683 | 0.9852 | Saussure | 0.983 |
| $\mathrm{C}_{2} \mathrm{H}_{2}$. | 26.02 | 0.8989 | 0.9056 | Ledue. | 0.992 |

a Landolt, H., and Börnstein, R.: Physikalisch-Chemische Tabellen, 1912, pp. 148, 149.

Molecular volumes of carbon dioxide at $20^{\circ}$ C. and various partial pressures.

| Pressure. | Molecular volume. | Percentage of total pressure. | Pressure. | Molecular volume. | Percentage of total pressure. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Mm. |  |  | Mm. |  |  |
| 200.. | 0.999 .999 | 26.3 | $600 .$. | O.997 | 65.8 78.9 |
| 300. | . 998 | 39.5 | 700. | . 995 | 91.9 |
| 400. | . 997 | 52.6 | 760. | . 995 | 100.0 |

In compiling the table of molecular volumes of carbon dioxide, advantage was taken of the work of Rayleigh ${ }^{a}$ and Chappuis ${ }^{b}$ on the coefficient of expansion of carbon dioxide. The specific gravity of carbon dioxide as given by Rayleigh was determined at $0^{\circ} \mathrm{C}$. and 760 mm . pressure. The value at $20^{\circ} \mathrm{C}$. and 760 mm . pressure was determined from the coefficient of expansion of carbon dioxide between $0^{\circ} \mathrm{C}$. and $20^{\circ} \mathrm{C}$.

The graph was plotted from two values determined experimentally, the value at $20^{\circ} \mathrm{C}$. and 760 mm . pressure and that at $20^{\circ} \mathrm{C}$. and 380 mm . pressure.

A tabulation of the molecular volumes of ethane at $0^{\circ} \mathrm{C}$. and various partial pressures follows:

Molecular volumes of ethane at $0^{\circ} \mathrm{C}$. and various partial pressures.

| Pressure. | Molecular volume. | Pressure. | Molecular volume. |
| :---: | :---: | :---: | :---: |
| Mm. |  | Mm. |  |
| 100 | 0.999 | 500 | 0.994 |
| 200 | . 997 | 600 | . 992 |
| 300 | . 996 | 700 | . 991 |
| 400 | . 995 | 760 | . 990 |
|  |  |  |  |

The coefficient of expansion of ethane between $0^{\circ} \mathrm{C}$. and $20^{\circ} \mathrm{C}$. has not been determined; consequently the same molecular volume was used at $20^{\circ} \mathrm{C}$., the ordinary laboratory temperature, as was determined by Baumé and Perrot at $0^{\circ} \mathrm{C}$. The resulting error can be disregarded without introducing any appreciable error in the analysis, judging from the case of the molecular volume of carbon dioxide which at $20^{\circ} \mathrm{C}$. is only 0.001 different from the value at $0^{\circ} \mathrm{C}$.

The values between 0.0 and 760 mm . pressure are interpolated from the values at 0.0 mm . and 760 mm ., which were determined experimentally.

From a careful search of the literature, the authors were unable to find any determination of the density of propane, but they have

[^2]information at hand that shows beyond doubt that, at $0^{\circ} \mathrm{C}$. and 760 mm . pressure, propane is by no means a perfect gas.

Following are some equations that hold only when the partial pressure of the combustible gas and that of the carbon dioxide (at $0^{\circ}$ and 760 mm .) produced by the combustion are 95 to 100 per cent of the total pressure. If the partial pressures differ from these, different molecular volumes, depending upon the partial pressures, are used.

Theoretical and corrected equations for combustion of certain gases.
CH $_{4}$, Theoretical Equation.
$\mathrm{CH}_{4}-2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{CH}_{4}$, Corrected Equation.
$0.999 \mathrm{CH}_{4}+2.000 \mathrm{O}_{2}=0.994 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
0.999 volumes +2.000 volumes $-0.99 \ddagger$ volumes $=2.005$ volumes $=$ contraction
0.498 contraction $=\mathrm{CH}_{4}$ $1.005 \mathrm{CO}_{2}=\mathrm{CH}_{4}$
$\mathrm{C}_{2} \mathrm{H}_{6}$, Theoretical Equation.
$\mathrm{C}_{2} \mathrm{H}_{6}+3.5 \mathrm{O}_{2}=2 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{C}_{2} \mathrm{H}_{6}$, Corrected Equition.
$0.990 \mathrm{C}_{2} \mathrm{H}_{6}+3.5 \mathrm{O}_{2}=1.988 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}$
0.990 volumes +3.5 volumes -1.985 volumes $=2.502$ volumes $=$ contraction
0.396 contraction $=\mathrm{C}_{2} \mathrm{H}_{6}$ $0.497 \mathrm{CO}_{2}=\mathrm{C}_{2} \mathrm{H}_{6}$

CO, Theoretical Equation.

$$
2 \mathrm{CO} \div \mathrm{O}_{2}=2 \mathrm{CO}_{2}
$$

CO, Corrected Equatton.
$2.000 \mathrm{CO}+1.000 \mathrm{O}_{2}=1.988 \mathrm{CO}_{2}$
2.000 volumes +1.000 volumes -1.988 volumes $=1.012$ volumes $=$ contraction
1.976 contraction $=\mathrm{CO}$
$1.006 \mathrm{CO}_{2}=\mathrm{CO}$
$\mathrm{C}_{3} \mathrm{H}_{8}$, Theoretical Eqcition.
$\mathrm{C}_{3} \mathrm{H}_{8}+5 \mathrm{O}_{2}=3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{C}_{3} \mathrm{H}_{8}$, Corrected Equation.
The observed density of propane, as iar as the authors were able to determine, has never been published.
$\mathrm{C}_{2} \mathrm{H}_{4}$, Theoretical Equation.
$\mathrm{C}_{2} \mathrm{H}_{4}+3 \mathrm{O}_{2}=2 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{C}_{2} \mathrm{H}_{4}$, Corrected Equation.
$0.983 \mathrm{C}_{2} \mathrm{H}_{4}+3.000 \mathrm{O}_{2}=1.988 \mathrm{CO}_{2}$
0.983 volumes +3.000 volumes -1.988 volumes $=1.995$ volumes $=$ contraction
0.493 contraction $=\mathrm{C}_{2} \mathrm{H}_{4}$
$0.494 \mathrm{CO}_{2}=\mathrm{C}_{2} \mathrm{H}_{4}$

$$
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{2}, \text { Theoretical Equation. } \\
\mathrm{C}_{2} \mathrm{H}_{2}+2.5 \mathrm{O}_{2}=2 \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \\
\mathrm{C}_{2} \mathrm{H}_{2}, \text { Corrected Equation. } \\
0.992 \mathrm{C}_{2} \mathrm{H}_{2}+2.5000 \mathrm{O}_{2}=1.988 \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \\
0.992 \text { volumes }+2.500 \text { volumes }-1.988 \text { volumes }=1.504 \text { volumes }=\text { contraction } \\
0.659 \text { contraction }=\mathrm{C}_{2} \mathrm{H}_{2} \\
0.499 \mathrm{CO}_{2}=\mathrm{C}_{2} \mathrm{H}_{2}
\end{gathered}
$$

## GAS-ANALYSIS APPARATUS USED BY THE AUTHORS.

The apparatus used by the authors for the analysis of natural gas and other combustible gases is shown in figure 1.


Figure 1.-Apparatus for analysis of combustible gases.

It consists of a $100-\mathrm{c}$. c. burette, which is graduated in tenths of 1 c. c. but can easily be read to 0.05 c. c. Mercury is used as the trapping fluid. At $f$ is the compensating tube. Both the burette and the compensating tube are contained in a water jacket. At $g$ is a mercury manometer.

Attached to the burette by means of rubber tubing is the train of stopcocks which are in turn connected to the caustic potash pipette $a$, the alkaline pyrogallate or phosphorous pipette $b$, the slow-combustion pipette $c$, and the alkaline pyrogallate pipette $d$, which contains a supply of nitrogen obtained by removing oxygen from air. The nitrogen is used to sweep out the capillary tubing before an analysis, thereby displacing gas left in the tubing from a previous analysis. Mercury is used in the slow-combustion pipette $c$.

## CORRECTION OF ANALYSES FOR MOLECULAR VOLUME.

The following tables containing the results of analyses of Pittsburgh natural gas, methane, and carbon monoxide will serve to show the magnitude of the errors introduced into the calculation from the combustion data when no account is taken of the true molecular volumes of the gases entering into the reactions.

Results of analyses of methane from different sources.

| Item. | Mine gas. |  |  |  |  | Methane prepared by method of Gladstone and Tribe. |  |  | Natural gas. |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Laboratory No. 1986. | Labo- <br> ratory No. 2492. | Laboratory No. 2781. | Laboratory No. 2990. | Laboratory No. 2481. | Sample 1. | Sample 2. | Sample 3. | Laboratory No. 3150. | Laboratory No. 3149. 3149. |
| Volume of sample taken, c. c.......... | 33.70 | 45. 75 | 38.70 | 42.30 | 43.70 | 42.00 | 31.40 | 47.15 | 41. 70 | 40.40 |
| Volumeafter carbon dioxide absorption, c.c........... | 33. 70 | 45.75 | 38.70 | 42.30 | 43. 70 | 41.95 | 31.40 | 47.15 | 41. 70 | 38.40 |
| Portion taken, c. c.. | 33.70 | 45.75 | 38.70 | 42.30 | 43.70 | 41.95 | 31.40 | 47.15 | 41. 70 | 33.40 |
| Oxygen added, c. c - | 95.65 | 70.10 | 68.05 | 51.10 | 46.90 | 99.10 | 71. 25 | 99.45 | 87.40 | 80.00 |
| Total volume, c.c... | 129.35 | 115.85 | 106.75 | 93.40 | 90.60 | 141.05 | 102.65 | 146.60 | 129.10 | 118. 40 |
| Volume after burning, c. c............ | 65.80 | 58.95 | 83.20 | 67.20 | 56. 80 | 59.50 | 40.85 | 53.85 | 60.05 | 56.05 |
| Contraction, c. c..... | 63.55 | 56.90 | 23.55 | 26.20 | 33.80 | 81.55 | 61.80 | 92.75 | 69.05 | 62.35 |
| Volume after absorption of carbon dioxide, c.c.......... | 34.30 | 30.65 | 71.40 | 54.15 | 39.90 | 18.90 | 10.15 | 7.90 | 25.75 | 25.05 |
| Carbon dioxide, c. c. | 31.50 | 28.30 | - 11.80 | 13.05 | 16.90 | 40.60 | 30.70 | 45.95 | 34.30 | 31.00 |
| Carbon dioxide, percentage of total pressure. | 47.9 | 47.9 | 14.2 | 19.4 | 29.7 | 68.2 | 75.1 | 85.3 | 57.1 | 55.3 |
| Molecular volume of carbon dioxide corrected from: |  |  |  |  |  |  |  |  |  |  |
| Table $a$.......... | 0.997 | 0.997 |  |  |  | 0.997 | 0.996 | 0.996 | 0.997 | 0.997 |
| Theoretical equation (one-half contraction minus carbon dioxide), c. c. - | 0.28 | 0.15 | $-0.02$ | 0.05 | 0.0 | 0.18 | 0.20 | 0.43 | 0.22 | 0.18 |
| Corrected equation (correction times contraction minus correction times carbon dioxide), c. c.. | 0.12 | 0.01 |  |  |  | -0.03 | +0.02 | 0.15 | +0.05 | 0.02 |
| Methane from uncorrected contraction, per cent..... | 94.3 | 62.2 | 30.5 | 31.0 | 38.7 | 97.1 | 98.4 | 98.4 | 82.8 | - 77.2 |
| Methane from uncorrected carbon dioxide, per cent. | 93.5 | 61.9 | 30.5 | 30.9 | 38.7 | 96.7 | 97.8 | 97.5 | 82.3 | 76. 7 |
| Difference, per cent. | 0.80 | 0.30 | 0.0 | 0.10 | 0.0 | 0.4 | 0.6 | 0.9 | 0.5 | 0.5 |
| Methane from corrected contraction, per cent...... | 94.1 | 62.0 |  |  |  | 96.90 | 98.2 | 98.2 | 82.60 | 77.0 |
| Methane from corrected carbon dioxide, per cent.... | 93.8 | 62.0 |  |  |  | 97.0 | 98.2 | 97.9 | 82.5 | 77.0 |
| Difference, per cent. | 0.30 | 0.0 |  |  |  | 0.10 | 0.0 | 0.3 | 0. 10 | 0.00 |

a See p. 10.

## Analyses of carbon monoxide a mixed with air.

| Item. | Sample- |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | 2 | 3 | 4 | 5 |
| Volume of sample taken, | 50.95 | 31.50 | 52.95 | 51.20 | 54.25 |
| Oxygen added, c. c...... | 39.50 | 77.90 | 35.40 | 36.15 | 47.40 |
| Total volume, c. c | 90.45 | 109.40 | 88.35 | 87.35 | 101.65 |
| $\backslash$ olume after burning, | 66.10 | 94.40 | 62.95 | 62. 60 | 75. 60 |
| Contraction, c. c.. | 24.35 | 15.00 | 25. 40 | 24. 75 | 26.05 |
| $V$ olume after absorption of carbon dioxide, | 17.80 | 64.40 | 12.75 | 13.85 | 23.90 |
| ( arbon dioxide, c. c.......................... | 48.30 | 30.00 | 50.20 | 48. 75 | 51.70 |
| ( arbon dioxide, percentage of total pressure ........ | 73.1 | 31.8 | 79.7 | 77.8 | 68.4 |
| Molecular volume of carbon dioxide corrected from: Table ${ }^{b}$ | 0.997 |  | 0.996 | 0.996 | 0.997 |
| Theoretical equation (two times contraction minus carbon dioxide) | 0.40 | 0.00 | 0.60 | 0.75 | 0.40 |
| Corrected equation (correction times contraction minus correction times carbon dioxide). | $-0.04$ | 0.00 | $-0.01$ | $+0.15$ | $-0.07$ |
| Carbon monoxide from uncorrected contraction, per cent. | 95.6 | 95.2 | 95.9 | 96.7 | 96.0 |
| Carbon monoxide from uncorrected carbon dioxide, per cent. | 94.8 | 95.2 | 94.8 | 95.2 | 95.3 |
| Difference, per cent . . . . . . . . . . . . . . . . . . . . . . . . . . . | 0.8 | 0.0 | 1.1 | 1.5 | 0.7 |
| Carbon monoxide from corrected contraction, per cent. | 95.1 |  | 95.2 | 95.9 | 95.5 |
| Carbon monoxide from corrected carbon dioxide, per cent | 95.0 |  | 95.2 | 95.6 | 95.6 |
| Difference, per cent | 0.1 |  | 0.0 | 0.3 | $-0.1$ |

a Prepared by the action of concentrated sulphuric acid on oxalic acid.
${ }^{6}$ See p. 10.

## Analyses of Pittsburgh natural gas

| Item. | Sample- |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | 2.16 .13 | 2.1.13 | 9.15 .12 | 12.1.12 |
| Volume of sample taken, c. c. | 31.20 | 31.55 | 30. 70 | 31.20 |
| Volume after carbon dioxide absorption, | 31.20 | 31.55 | 30. 70 | 31.20 |
| Part taken, e. c.... | 31.20 91.90 | 92.80 | 30.70 95.20 | 31.20 90.15 |
| Total volume, c. c | 123.10 | 124.35 | 125.90 | 121.35 |
| Volume after burning, | 58.10 | 58.60 | 62.30 | 56.45 |
| Contraction, c.c. | 65.00 | 65.75 | 63.60 | 64.90 |
| Volume after carbon dioxide absorption, e. | 21.90 | 22.00 | 27.10 | 20.45 |
| Carbon dioxide. | 36.20 | 36.60 | 35. 20 | 36.00 |
| Methane from theoretical equation, per cent. | 84.4 | 84.5 | 85.1 | 85.1 |
| Ethane from theoretical equation, per cent. | 15.8 | 15.8 | 14.8 | 15.2 |
| Total paraffins from theoretical equation, per cent | 100.2 | 100.3 | 99.9 | 100.3 |
| Methane from corrected equation, per cent. | 83.6 | 83.7 | 84.3 | 84.3 |
| Ethane from corrected equation, per cent. | 16.3 | 16.2 | 15.2 | 15.7 |
| Total paraffins from corrected equation, per cent. | 99.9 | 99.9 | 99.5 | 100.0 |
| Difference, total paraffins theoretical minus corrected | 0.3 | 0.4 | 0.4 | 0.3 |

The values for natural gas are calculated by use of the formulas following. The ordinary equations in which $x$ represents partial methane and $y$ partial ethane serve to obtain the partial pressures of the constituents closely enough for the author's purposes.

## Hence:

$$
\begin{aligned}
2 x+2.5 y & =\text { contraction } \\
x+2.0 y & =\text { carbon dioxide produced }
\end{aligned}
$$

From which $x$ and $y$ are calculated.
The partial pressure of the carbon dioxide is obtained in all analyses by dividing the carbon dioxide produced by the combustion by the volume after burning and multiplying the result by 760 .

The corrected equations take the following form for these particular calculations:

$$
\begin{aligned}
& 2.003 x+2.5 y=\text { contraction } \\
& 0.997 x+2.0 y=\text { carbon dioxide produced }
\end{aligned}
$$

From which $x$ and $y$ are calculated.
It will be noticed that the molecular volumes of the ethane and of the carbon dioxide produced from it alone have been taken as 1.000 , because the partial pressures of the gases are so low that no appreciable error is introduced into the calculation by this procedure. However, if the ethane as shown by the ordinary equations were 25 per cent or higher, as is the case in many natural gases, suitable corrections would have to be made for the molecular volumes of ethane of and carbon dioxide produced by its combustion.

## PUBLICATIONS ON MINE ACCIDENTS AND METHODS OF MINING.

The following Bureau of Mines publications may be obtained free by applying to the Director, Bureau of Mines, Washington, D. C.

Bulletin 10. The use of permissible explosives, by J. J. Rutledge and Clarence Hall. 1912. 34 pp., 5 pls., 4 figs.
Bulletin 15. Investigations of explosives used in coal mines, by Clarence Hall, W. O. Snelling, and S. P. Howell, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by C. E. Munroe. 1911. 197 pp., 7 pls., 5 figs.

Bulletin 17. A primer on explosives for coal miners, by C. E. Munroe and Clarence Hall. 61 pp., 10 pls., 12 figs. Reprint of United States Geological Survey Bulletin 423.

Bulletin 20. The explosibility of coal dust, by G. S. Rice, with chapters by J. C. W. Frazer, Axel Larson, Frank Haas, and Carl Scholz. 204 pp., 14 pls., 28 figs. Reprint of United States Geological Survey Bulletin 425.

Bulletin 44. First national mine-safety demonstration, Pittsburgh, Pa., October 30 and 31, 1911, by H. M. Wilson and H. H. Fay, with a chapter on the explosion at the experimental mine, by G. S. Rice. 1912. 75 pp., 7 pls., 4 figs.

Bulletin 45. Sand available for filling mine workings in the Northern Anthracite Coal Basin of Pennsylvania, by N. H. Darton. 1913. 33 pp., 8 pls., 5 figs.

Bulletin 46. An investigation of explosion-proof mine motors, by H. H. Clark. 1912. 44 pp., 6 pls., 14 figs.

Bulletin 48. The selection of explosives used in engineering and mining operations, by Clarence Hall and S. P. Howell. 1913. 50 pp., 3 pls., 7 figs.

Bulletin. 52. Ignition of mine gases by the filaments of incandescent electric lamps, by H. H. Clark and L. C. Ilsley. 1913. 31 pp., 6 pis., 2 figs.

Bulletin 53. Mining and treatment of feldspar and kaolin in the Southern Appalachian region, by A. S. Watts. 1913. 171 pp ., 16 pls., 12 figs.

Bulletin 56. First series of coal-dust explosion tests in the experimental mine, by G. S. Rice, L. M. Jones, J. K. Clement, and W. L. Egy. 1913.115 pp., 28 figs.

Bulletin 59. Investigations of detonators and electric detonators, by Clarence Hall and S. P. Howell. 1913. $73 \mathrm{pp} ., 7$ pls., 5 figs.

Bulletin 65. Oil and gas wells through workable coal beds; papers and discussions, by G. S. Rice, O. P. Hood, and others. 1913. 101 pp., 1 pl., 11 figs.

Technical Paper 6. The rate of burning of fuse as influenced by temperature and pressure, by W. O. Snelling and W. C. Cope. 1912. 28 pp.

Technical Paper 7. Investigations of fuse and miners' squibs, by Clarence Hall and S. P. Howell. 1912. 19 pp .

Technical Paper 11. The use of mice and birds for detecting carbon monoxide after mine fires and explosions, by G. A. Burrell. 1912. 15 pp .
Technical Paper 13. Gas analysis as an aid in fighting mine fires, by G. A. Burrell and F. M. Seibert. 1912. 16 pp., 1 fig.
Technical Paper 14. Apparatus for gas-analysis laboratories at coal mines, by G. A. Burrell and F. M. Seibert. 1913. 24 pp., 7 figs.

Technical Paper 17. The effect of stemming on the efficiency of explosives, by W. O. Snelling and Clarence Hall. 1912. 20 pp., 11 figs.

Technical Paper 18. Magazines and thaw houses for explosives, by Clarence Hall and S. P. Howell. 1912. 34 pp., 1 pl., 5 figs.
Technical Paper 19. The factor of safety in mine electrical installations, by H. H. Clark. 1912. 14 pp .

Technical Paper 21. The prevention of mine explosions; report and recommendations, by Victor Watteyne, Carl Meissner, and Arthur Desborough. 12 pp. Reprint of United States Geological Survey Bulletin 369.
Technical Paper 22. Electrical symbols for mine maps, by H. H. Clark. 1912. 11 pp., 8 figs.
Technical Paper 24. Mine fires, a preliminary study, by G. S. Rice 1912: 51 pp., 1 fig.
Technical Paper 28. Ignition of mine gas by standard incandescent lamps, by H. H. Clark. 1912. 6 pp.

Technical Paper 29. Training with mine-rescue breathing apparatus, by J. WPaul. 1912. 16 pp .
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Technical Paper 40. Metal-mine accidents in the United States during the calendar year 1911, compiled by A. H. Fay. 1913. 54 pp.
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Technical Paper 52. Permissible explosives tested prior to March 1, 1913, by Clarence Hall. 1913. 11 pp.
Miners' Circular 3. Coal-dust explosions, by G. S. Rice. 1911. 22 pp.
Miners' Circular 4. The use and care of mine-rescue breathing apparatus, by J. W. Paul. 1911. 24 pp., 5 figs.

Miners' Circular 5. Electrical accidents in mines; their causes and prevention, by H. H. Clark, W. D. Roberts, L. C. Ilsley, and H. F. Randolph. 1911. 10 pp., 3 pls.
Miners' Circular 6. Permissible explosives tested prior to January 1, 1912, and precautions to be taken in their use, by Clarence Hall. 1912. 20 pp .

Miners' Circular 9. Accidents from falls of roof and coal, by G. S. Rice. 1912. 16 pp .

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Miners' Circular 12. The use and care of miners' safety lamps, by J. W. Paul. 1913. 16 pp., 4 figs.


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